JOC Article

Studies on the Reactivity of Aryliodonium Ylides of 2-Hydroxy-1,4-naphthoquinone: Reactions with Amines

Elizabeth Malamidou-Xenikaki, Spyros Spyroudis,* and Maria Tsanakopoulou

Laboratory of Organic Chemistry, Department of Chemistry, University of Thessaloniki, Thessaloniki 54124, Greece

sspyr@chem.auth.gr

Received March 20, 2003

Aryliodonium ylides of 2-hydroxy-1,4-naphthoquinone react with amines in refluxing dichloromethane to afford good yields of indanedione 2-carboxamides **5**, through a ring-contraction and α,α′-dioxoketene formation reaction. These amides exist in solution in an unusual enol−amide form. In contrast, the same reactants in a copper-catalyzed reaction afford arylamines and 3-iodo-4-hydroxy-1,2-naphthoquinone.

Introduction

Quinones with hydroxy groups attached directly to the quinone ring are found in nature in great variety, and most of them exhibit interesting biological activity.[1] This activity, combined with the diversity in their chemical behavior, make them attractive targets in organic synthesis. The synthesis and reactivity of hydroxyquinones have recently been reviewed.[2]

An important strategy for the use of hydroxyquinones in synthesis is the functionalization of the position next to the hydroxy group. This can be achieved with different methodologies,[2] but there is always the need for a group that can activate this position in a broad spectrum of reactions. The aryliodonio group plays such a role. Hydroxyquinones **1** react most easily with (diacetoxyiodo)arenes to afford good to excellent yields of 2-oxido-3-phenyliodonio-1,4-quinones or aryliodonium ylides of hydroxyquinones (**2**) (Scheme 1).

These ylides are labile compounds as the aryliodonio group easily departs to give rise to a variety of products depending on the reaction conditions. They react with hydrohalogen acids to furnish halogenated hydroxyquinones,[3] and they afford transylidation products[3] and various cyclization products from photochemically induced reactions with alkenes, alkynes, and carbon disulfide.[3] 3-Phenyliodonium ylides of 2-hydroxy-1,4-naphthoquinone (lawsone) and derivatives afford furoquinones in a Pd- or Cu-catalyzed cyclization reaction with terminal acetylenes.[4] The same ylides were used for the regiospecific synthesis of unsymmetrical 2,3-diarylquinones via a stepwise Pd(0)-catalyzed coupling with arylstannanes[5] and for the

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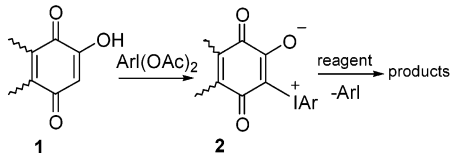

synthesis of 2,3-dihalonaphthoquinones[6] in studies toward the synthesis of conocurvone, a trimeric hydroxynaphthoquinone and potential anti-HIV agent. Thermal treatment of hydroxyquinones affords cyclopentenediones[7] through ring contraction, and this reaction found applications in the preparation of cyclopentenediones bearing the interesting triptycene moiety.[8]

Continuing our studies on the chemistry of aryliodonium ylides[9] we investigated the reactivity of the title ylides toward amines. It must be noted that the reaction of amines with hydroxyquinone model compounds has been studied in detail since topaquinones (compounds with the hydroxyquinone moiety) are the redox-active organic cofactors for the copper amine oxidases catalyzed deamination of various amines.[10,11]

Results and Discussion

The reaction of phenyliodonium ylide of 2-hydroxy-1,4-naphthoquinone[3] (**3**) with a variety of amines **4** under different reaction conditions was investigated. No reaction was observed when a suspension of **3** in CH_2Cl_2 with an equimolecular amount of amine was stirred for a long period at room temperature. The same mixture brought

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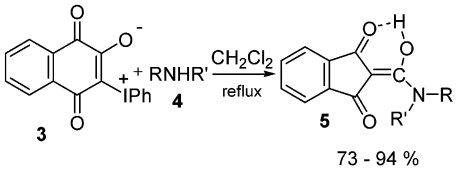
(11) Lee, Y.; Ling, K.-Q.; Lu, X.; Silverman, R. B.; Shepard, E. M.; Dooley, D. M.; Sayre, L. M. *J. Am. Chem. Soc*. **2002**, *124*, 12135.

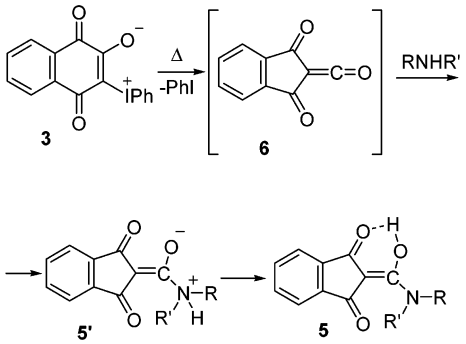
10.1021/jo0343679 CCC: $25.00
Published on Web 06/06/2003

SCHEME 2[a]



[a] Key: **4**, **5a**, R = Ph, R′ = H; **4**, **5b**, R = *p*-Me-C_6H_4, R′ = H; **4**, **5c**, R = *p*-OMe-C_6H_4, R′ = H; **4**, **5d**, R = *p*-$NO_2C_6H_4$, R′ = H; **4**, **5e**, R = *o*-Me-C_6H_4, R′ = H; **4**, **5f**, R = $PhCH_2$, R′ = H; **4**, **5g**, R = $PhCH_2CH_2$, R′ = H; **4**, **5h**, R = Ph, R′ = CH_3; **4**, **5i**, R = R′ = Ph.

SCHEME 3

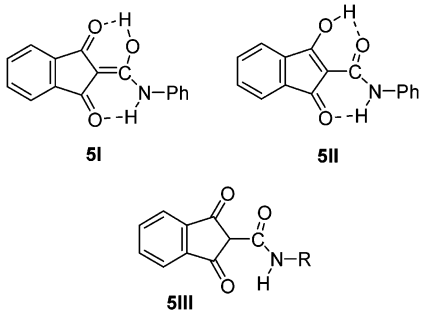


at reflux for 4−7 h afforded very good yields of indanedione carboxamides **5** in a clean reaction (Scheme 2). Amides **5** were conveniently isolated from the reaction mixture by crystallization. Attempts to remove unreacted amines and the iodobenzene main byproduct by chromatographic separation led to the conversion of **5** into high-temperature melting compounds that were insoluble in most common solvents.

The reaction proceeds through expulsion of iodobenzene, carbene formation, and Wolff rearrangement of the latter to α,α′-dioxoketene **6**, a reaction pathway that has been proposed for the ring contraction of analogous ylides to cyclopentenedione derivatives.[7,8] Ketene **6** reacts with amine to afford the corresponding amide **5** (Scheme 3). The latter exists in solution exclusively in an unusual enol−amide form **5**.

The isolation of **5** is another evidence for the thermal decomposition of ylide **3** to the intermediate α,α′-dioxoketene **6**. Such species are highly reactive,[12a] and only a few bearing mostly bulky substituents have been isolated.[12b]

It has also been shown that the reaction of amines with ketenes generally[13a] and with α-oxoketenes specifically[13b] proceeds through zwitterionic species such as **5′** that tautomerize to enols of amides such as **5** initially, and to amides finally. In our case, it is most possible that the enol−amide form is stabilized by the hydrogen bond formed between the enolic hydrogen and the carbonyl of the indanedione ring. A second hydrogen bond between the amidic hydrogen and the other carbonyl group, in cases where R′ = H, also contributes to the stabilization of the enol form.



The stabilization of enols of carboxylic acid amides with β-electron-withdrawing substituents has been extensively investigated by Rappoport in a series of papers.[14] It was found that the degree of enolization depends on the nature of the substituents and varies if it is measured in the solid state or in solution and that the nature of the solvent ($Cl_2CDCDCl_2$, CD_3CN, $CDCl_3$, and DMSO) plays also some role. It was also found that the δ values in the solid-state ^{13}C spectra are similar to those in $CDCl_3$ and DMSO, suggesting a similar structure in solution and in the solid state. In our case, ^1H and ^{13}C NMR spectroscopy (in $CDCl_3$) show clearly that in solution amides **5** exist exclusively in enol form, with OH and NH resonating as broad 1H signals at 9.50−11.80 and 7.90−9.50 ppm, respectively. Both signals exchange with D_2O according to analogous observations.[14a] Moreover, the lack of a peak around 4.40−4.50 ppm excludes a C−H bond at the carbon between the two carbonyls at indanedione ring, thus excluding the amide form **5III**. The same carbon in ^{13}C NMR appears at 95−96 ppm, instead of a calculated and observed value of ∼60 ppm for C−H of the amide form.[14a] The relatively upfield appearance of enolic hydrogen (9.50−11.80 ppm) compared to other amide−enol analogous systems (15−17 ppm)[14a] may be attributed to O−O distance. Indeed, this distance, playing an important role for the strength of hydrogen bond,[14a] in **5I** is calculated to be ∼2.72 Å (∼2.77 Å for **5II**) compared to distances 2.44−2.50 Å calculated (and found in one case) for the above-mentioned analogous systems.[14a]

Although it is difficult to distinguish between the two enolic structures **5I** and **5II**, we believe that spectroscopic data are more in agreement with **5I**. Moreover, in a recently published paper[15] reporting the reaction of enols of amides with diazomethane, it is mentioned that in the solid state 2-anilido-1,3-indanedione exists as the enol **5a** (a statement probably based on X-ray structure data), thus strengthening our assumption.

It is obvious that the NH group, forming also a hydrogen bond with the second carbonyl group, contributes to the stabilization of the enol structure. In the case of the reaction of **3** with *N*-methylaniline **(4h),** the resulting **5h**, lacking the NH group, is rather unstable. In solution, it exists as a mixture of amidic−enolic form 2.5:1 (estimated by ^1H NMR) and was easily hydrolyzed to a mixture of indandione and *N*-methylaniline. In an analogous reaction with diphenylamine, the correspond-

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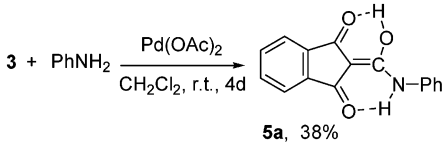
(15) Lei, Y. X.; Rappoport, Z. *J. Org. Chem*. **2002**, *67*, 6971.

SCHEME 4



SCHEME 5

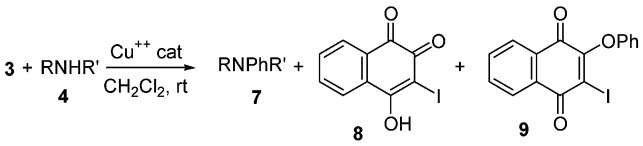


TABLE 1. Products from the Copper-Catalyzed Reaction of Ylide 3 with Amines

amine **4**	amine **7**, %	iodoquinone **8**, %	iodoether **9**, %
4a	60	48	32
4b	55	38	11
4c[a]	43	35	16
4d	6	traces	9
4e	47	40	7
4f	38		traces
4g[b]	30	55	18
4h	66	50	21

[a] A small yield of lawsone was also isolated. [b] A 5% yield of diphenylated amine, $Ph_2NCH_2CH_2Ph$, was isolated.

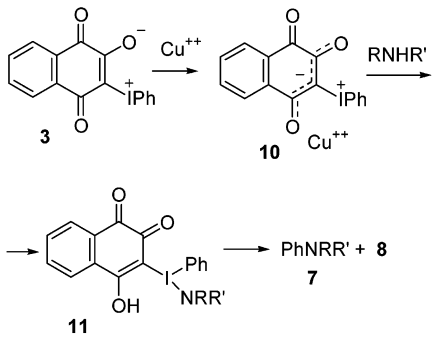
ing diphenyl derivative **5i** was not isolated at all, although the reaction seemed to proceed in the usual way, with consumption of both amine and ylide. The yellow product initially formed rapidly decomposed to indanedione and diphenylamine during the isolation procedure.

Finally, it was found that the formation of enol−amides **5** takes place even at room temperature in the presence of a catalytic amount of $Pd(OAc)_2$, although the reaction is considerably slower (Scheme 4). Obviously, Pd facilitates the fission of C−I bond and the formation of α,α′-dioxoketene **6**. An analogous catalytic action of Pd has been observed in the coupling reaction of ylide **3** with terminal acetylenes.[4]

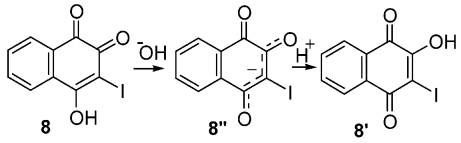
Whereas the thermal (or Pd-catalyzed) reaction of ylide **3** with amines affords ring-contraction products, the corresponding Cu-catalyzed reaction leads to phenylated amines and retention of the quinone moiety (Scheme 5). Overnight stirring of a suspension of equimolecular amounts of ylide **3** and the corresponding amine **4** in CH_2Cl_2 in the presence of a catalytic amount of $Cu(CF_3SO_3)_2$ at room temperature afforded phenylated amines **7**, 3-iodo-4-hydroxy-1,2-naphthoquinone **(8),** and 2-phenoxy-3-iodo-1,4-naphthoquinone **(9)** as the main products (Scheme 5 and Table 1).

It is most possible that arylamines **7**, as well as iodohydroxyquinone **8**, formed in roughly equivalent yields, are the degradation products of the intermediary iodane **11**. This is a well-known reaction pathway for various iodans formed from the reaction of hypervalent iodine reagents with the appropriate substrates.[16] As far as the catalytic role of copper is concerned, it is reasonable to assume that copper ions form with ylide **3** enolates

SCHEME 6



SCHEME 7



of type **10**, thus increasing the electrophilic character of iodine and accelerating the nucleophilic attack of amine to iodine to form **11** (Scheme 6). The formation of enolates analogous to **10** was also proposed as the first step of the copper amine oxidase catalyzed reaction of topaquinones with amines.[17] The proposed reaction pathway seems reasonable, although an aromatic nucleophilic substitution route cannot be excluded. It must be noted that other Cu^{2+} reagents, e.g., $Cu(acac)_2$, catalyzed in the same manner the reaction of **3** with amines, but yields were considerably lower.

According to the proposed above reaction pathway, the nucleophilicity of amine plays important role. Indeed, the reaction with *N*-methylaniline **(4h)** gave the best yield of phenylated amine, in contrast to *p*-nitroaniline **(4d)**.

The isolation of 3-iodo-4-hydroxy-1,2-naphthoquinone **(8)** from the above reaction is most interesting. Hydroxyquinones invariably exist in the *p*-quinone tautomeric form, and only in a few cases cyclization products having the *o*-quinone structure were isolated.[2] It is possible that the *o*-quinone form is more stable in iodane **11** and hence the formation of **8**. When **8** was dissolved in alkali the more stable *p*-quinone **8′** was precipitated upon acidification, presumably through the enolic form **8″** (Scheme 7).

The formation of iodo phenyl ether **9** from the Cu-catalyzed reaction of **3** with amines is also of interest. Such ethers are the result of thermal phenyl (or aryl) migration from iodine to oxygen that has been observed in a variety of phenyl (or aryl) iodonium ylides,[16] but not in those derived from hydroxyquinones. In the latter case, under thermal conditions, the fission of iodine−quinonic carbon bond with expulsion of iodobenzene always occurs. The isolation of **9** in considerable amounts from almost all the reactions with amines (Table 1) verifies the initial formation of copper enolates of type **10**, which, by strengthening the mentioned I−C bond, facilitate phenyl migration.

To find out in which position of the phenyl ring amination takes place, the *p*-tolyliodonium ylide of law-

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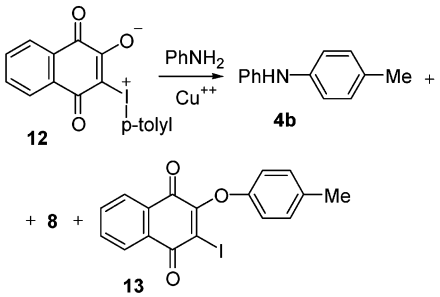
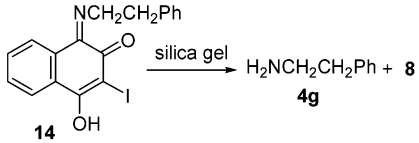
SCHEME 8



SCHEME 9



sone **(12)** was prepared. The copper-catalyzed reaction of **12** with aniline afforded *N*-phenyl-*p*-tolylamine **(4b)**, **8**, and the corresponding *p*-tolyl ether **13**, thus verifying that both amination and aryl migration take place at the carbon ipso to iodine (Scheme 8).

Finally, in one case, namely the reaction of **3** with *β*-phenylethylamine **(4g)**, a red solid was crystallized out from the reaction mixture. On the basis of spectroscopic and analytical data, this solid proved to be imine **14** in 18% yield. On passing **14** through a silica gel column, it was hydrolyzed to hydroxyiodoquinone **8** and initial amine **4g (**Scheme 9**)**. This finding indicates that also in other reactions with amines analogous imines may have been formed but not detected. This assumption also explains the fact that, although the amine is consumed toward the end of the reaction (checked by TLC in the reaction mixture), yields of arylated amines are not very high.

In conclusion, the reaction of iodonium ylides of hydroxyquinones with amines follows two different reaction pathways: Under thermal conditions (or Pd catalysis), good yields of indanedione carboxamides are isolated through the intermediacy of highly active α,α′-dioxoketene. These carboxamides exist in the interesting enol−amide structure. In the Cu^{2+}-catalyzed corresponding reactions, arylation of the amine takes place in moderate yields. Iodoquinone **8**, bearing a most unusual for hydroxyquinones *o*-quinonic structure, is also isolated from the same reactions.

Experimental Section

General Procedure for the Thermal Reaction of 3 with Amines. A suspension of 2-oxido-3-phenyliodonio-1,4-naphthoquinone **(3)**[3] (1 mmol) and the corresponding amine **4** (1 mmol) in CH_2Cl_2 (15 mL) was refluxed for 4−7 h until a clear solution resulted and TLC showed the disappearance of ylide **3**. The solution was concentrated in a vacuum to half its volume, hexanes (∼10 mL) was added, and the precipitated yellow solid was filtered and washed repeatedly with hexanes. An analytical sample was obtained by recrystallization from CH_2Cl_2−hexanes. For simplicity reasons, compounds **5** are named according to their amide tautomeric form (e.g., compound **5a** in its enol−amide form should be named 2-[anilino(hydroxy)methylidene]-1*H*-indene-1,3(2*H*)-dione).

1,3-Dioxo-*N*-phenyl-2-indancarboxamide (5a): yield 84%; mp 144−146 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) *δ* 11.87 (s, br, 1H), 9.51 (s, br, 1H), 7.65−7.49 (m, 6H), 7.38 (t, J = 7 Hz, 2H), 7.20 (t, J = 7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) *δ* 192.7, 190.3, 165.2, 137.5, 137.3, 135.6, 133.4, 133.1, 129.3, 125.6, 121.9, 121.5, 121.0, 96.0; MS *m*/*z* 265 (M^+, 91), 173 (84), 146 (19), 93 (100). Anal. Calcd for $C_{16}H_{11}NO_3$: C, 72.45; H, 4.18; N, 5.28. Found: C, 72.21; H, 4.21; N, 5.38.

1,3-Dioxo-*N*-(*p*-tolyl)-2-indancarboxamide (5b): yield 94%; mp 167−170 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) *δ* 10.80 (s, br, 1H), 9.52 (s, br, 1H), 7.70−7.54 (m, 4H), 7.40 (d, J = 8 Hz, 2H), 7.19 (d, J = 8 Hz, 2H), 2.36 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) *δ* 193.2, 190.4, 165.2, 137.7, 135.7, 133.4, 133.0, 132.9, 129.9, 121.9, 121.5, 121.2, 95.6, 21.0; MS *m*/*z* 279 (M^+, 87), 173 (76), 146 (14), 107 (95), 106 (100). Anal. Calcd for $C_{17}H_{13}NO_3$: C, 73.11; H, 4.69; N, 5.02. Found: C, 73.03; H, 4.51; N, 4.89.

1,3-Dioxo-*N*-(*p*-methoxyphenyl)-2-indancarboxamide (5c): yield 75%; mp 140−143 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) *δ* 9.50 (s, br, 1H), 7.84 (s, br, 1H), 7.68−7.53 (two overlapping m, 4H), 7.42 (d, J = 9 Hz, 2H), 6.91 (d, J = 9 Hz, 2H), 3.82 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) *δ* 193.2, 190.4, 165.0, 157.6, 137.8, 133.4, 133.0, 128.3, 123.0, 121.9, 121.4, 116.6, 114.5, 95.4, 55.5; MS *m*/*z* 295 (M^+, 44), 173 (53), 146 (18), 123 (85). Labile compound. No satisfactory elemental analysis could be obtained.

1,3-Dioxo-*N*-(*p*-nitrophenyl)-2-indancarboxamide (5d): yield 89%; mp 248−250 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) *δ* 9.61 (s, br, 1H), 8.27 (d, J = 8 Hz, 2H), 7.79 (d, J = 8 Hz, 2H), 7.65−7.57 (m, 5H); ^{13}C NMR ($CDCl_3$ + DMSO-d_6, 75 MHz) *δ* 193.9, 190.0, 162.8, 158.9, 96.4. Due to solubility reasons, the solution was heated in order to dissolve and partially decomposed to give two many peaks in the aromatic region: MS *m*/*z* 310 (M^+, 61), 173 (82), 146 (8), 138 (100). Anal. Calcd for $C_{16}H_{10}N_2O_5$: C, 61.94; H, 3.25; N, 9.03. Found: C, 61.56; H, 3.55; N, 8.93.

1,3-Dioxo-*N*-(*o*-tolyl)-2-indancarboxamide (5e): yield 97%; mp 163−165 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) *δ* 9.63 (s, br, 1H), 8.17 (s, br, 1H), 7.82 (d, J = 7 Hz, 1H), 7.65−7.52 (m, 4H), 7.31−7.21 (m, 2H), 7.15 (t, J = 7 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) *δ* 193.1, 190.6, 165.4, 137.7, 133.8, 133.5, 133.1, 130.9, 129.5, 126.9, 126.1, 122.7, 121.9, 121.6, 95.9, 17.8; MS *m*/*z* 279 (M^+, 100), 173 (90), 146 (16), 107 (87). Anal. Calcd for $C_{17}H_{13}NO_3$: C, 73.11; H, 4.69; N, 5.02. Found: C, 73.33; H, 4.56; N, 4.71.

1,3-Dioxo-*N*-benzyl-2-indancarboxamide (5f): yield 73%; mp 150−152 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) *δ* 10.24 (s, br, 1H), 8.19 (s, br, 1H), 7.63−7.58 (m, 2H), 7.54−7.49 (m, 2H), 7.41−7.29 (m, 5H), 4.63 (s, 1H), 4.61 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) *δ* 193.3, 190.2, 167.1, 138.1, 136.2, 133.0, 131.9, 128.9, 128.1, 127.6, 121.4, 94.4, 43.5; MS *m*/*z* 279 (M^+, 57), 173 (25), 146 (43), 107 (69), 106 (100). Anal. Calcd for $C_{17}H_{13}NO_3$: C, 73.11; H, 4.69; N, 5.02. Found: C, 72.95; H, 4.45; N, 5.05.

1,3-Dioxo-*N*-(2′-phenylethyl)-2-indancarboxamide (5g): yield 88%; mp 165−167 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) *δ* 10.67 (s, br, 1H), 7.93 (s, br, 1H), 7.64−7.57 (m, 2H), 7.55−7.48 (m, 2H), 7.37−7.18 (m, 5H), 3.70 and 3.68 (two t overimposed, J_1 = J_2 = 7 Hz, 2H), 2.94 (t, J = 7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) *δ* 193.3, 190.2, 167.1, 138.3, 137.5, 132.9, 128.9, 128.7, 127.0, 121.3, 93.9, 41.1, 35.7; MS *m*/*z* 293 (M^+, 70), 173 (100), 146 (33), 121 (11), 120 (43). Anal. Calcd for $C_{18}H_{15}NO_3$: C, 73.71; H, 5.15; N, 4.78. Found: C, 73.92; H, 4.91; N, 4.45.

1,3-Dioxo-*N*-[(phenyl)(methyl)]-2-indancarboxamide (5h): yield 79%; mp 127−130 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) *δ* 13.87 (s, br, 0.4H, enolic form), 8.01−7.92 (m, 2H), 7.85−7.78 (m, 2H), 7.60−7.25 (m, aromatic H for both forms), 4.21 (s, 1H), 3.64(s, 1.2H, Me for the enolic form), 3.37 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) *δ* characteristic peaks 194.5, 168.1, 164.7, 95.8, 58.8, 40.6, 37.5 (both forms); MS *m*/*z* 279 (M^+, 58), 173 (31), 146 (56), 108 (100), 107 (53). Labile compound. No satisfactory elemental analysis could be obtained.

General Procedure for the Cu-Catalyzed Reaction of 3 with Amines. A suspension of 2-oxido-3-phenyliodonio-1,4-naphthoquinone **(3)** (1 mmol), the corresponding amine **4** (1

mmol), and a catalytic amount of $Cu(CF_3SO_3)_2$ (20 mg, 0.055 mmol) in CH_2Cl_2 (15 mL) was stirred at rt overnight. The resulting clear solution was concentrated and chromatographed on column (silica gel, hexanes−ethyl acetate, 10:1, gradually increasing to pure ethyl acetate for the elution of **8**) to afford in order of eluance iodobenzene, arylamine **7**, iodo ether **9**, and finally hydroxyiodoquinone **8**.

All arylamines **7** were known compounds and were identified by comparison of their spectroscopic data with those of the literature.

2-Phenoxy-3-iodo-1,4-naphthoquinone (9): mp 161−164 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.26−8.18 (m, 1H), 8.07−7.99 (m, 1H), 7.81−7.71 (m, 2H), 7.41−7.30 (m, 2H), 7.16 (t, J = 7 Hz, 1H), 7.02 (d, J = 9 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 179.9, 176.2, 160.9, 156.3, 134.4, 134.3, 130.4, 129.8, 128.0, 127.4, 124.0, 116.6, 111.5; MS m/z 376 (M^+, 81), 250 (41), 165 (50), 77 (100). Anal. Calcd for $C_{16}H_9IO_3$: C, 51.09; H, 2.41. Found: C, 49.84; H, 2.62.

3-Iodo-4-hydroxy-1,2-naphthoquinone (8): mp 169−171 °C, crystallization from the reaction mixture (>300 °C isolation by column chromatography, silica gel−ethyl acetate); ^{1}H NMR ($CDCl_3$−DMSO-d_6, 300 MHz) δ 8.01 (d, J = 8 Hz, 1H), 7.92 (d, J = 8 Hz, 1H), 7.31 (t, J = 8 Hz, 1H), 7.22 (t, J = 8 Hz, 1H); ^{13}C NMR ($CDCl_3$-DMSO-d_6, 75 MHz) δ 183.6, 177.1, 170.6, 134.4, 134.1, 131.1, 130.1, 126.4, 126.2, 86.5; MS m/z 300 (M^+, 91), 272 (52), 273 (81). Anal. Calcd for $C_{10}H_5IO_3$: C, 40.03; H, 1.68. Found: C, 40.32; H, 1.91.

Isomerization of 8 to *p*-Quinone Isomer 8′. 3-Iodo-4-hydroxy-1,2-naphthoquinone **(8)** (30 mg, 0.1 mmol) was dissolved in a solution of 5% NaOH (4 mL), and the solution was acidified with concentrated HCl acid. The resulting suspension was extracted with CH_2Cl_2 (3 × 10 mL), dried, and concentrated to afford quantitatively 3-iodo-2-hydroxy-1,4-naphthoquinone **(8′)** in all respects identical with a sample prepared by an alternative route (reaction of HI acid with ylide **3**).[3]

2-Oxido-3-(*p*-tolyliodonio)-1,4-naphthoquinone (12). Ylide **12** was prepared by the same procedure as **3**,[3] using (diacetoxyiodo)-*p*-toluene instead of (diacetoxyiodo)benzene: mp 131−133 °C; ^{1}H NMR ($CDCl_3$−DMSO-d_6, 300 MHz) δ 8.10−8.07 (m, 1H), 8.04−8.00 (m, 1H), 7.72 (d, J = 7 Hz, 2H), 7.67−7.58 (m, 2H), 7.12 (d, J = 7 Hz, 2H), 2.27 (s, 3H). Anal. Calcd for $C_{17}H_{11}IO_3$: C, 52.33; H, 2.84. Found: C, 52.11; H, 2.82.

2-(*p*-Tolyloxy)-3-iodo-1,4-naphthoquinone (13): mp 175−178 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.24−8.17 (m, 1H), 8.05−7.97 (m, 1H), 7.78−7.65 (m, 2H), 7.13 (d, J = 7 Hz, 2H), 6.92 (d, J = 7 Hz, 2H), 2.32 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 179.8, 176.3, 161.0, 154.3, 134.3, 134.2, 133.6, 130.8, 130.4, 130.3, 128.0, 127.4, 116.5, 111.1, 20.8; MS m/z 390 (M^+, 76), 263 (100), 178 (82). Anal. Calcd for $C_{17}H_{11}IO_3$: C, 52.33; H, 2.84. Found: C, 52.21; H, 2.67.

***Z*,*E*-3-Iodo-4-hydroxy-1-[(2-phenylethyl)imino]-2-naphthalenone (14):** mp 169−171 °C; ^{1}H NMR ($CDCl_3$−DMSO-d_6, 300 MHz) δ 8.00−7.83 (m, 2H), 7.66−7.53 (m, 2H), 7.34−7.28 (m, 5H), 3.16−3.02 (m, 2H), 2.97−2.83 (m, 2H); ^{13}C NMR ($CDCl_3$−DMSO-d_6, 75 MHz) δ 181.9, 176.5, 170.2, 136.8, 133.9, 133.0, 130.3, 130.1, 128.3, 128.2, 126.3, 125.7, 125.5, 87.2 (br), 40.3, 33.0; MS m/z no M^+, 300 (82), 272 (52), 173 (71), 145 (45), 105 (77). Anal. Calcd for $C_{18}H_{14}NIO_2$: C, 53.62; H, 3.50; N, 3.47. Found: C, 53.57; H, 3.77; N, 3.37.

JO0343679